CRYSTAL FIELD THEORY OF Cu^{++} ION IN THE MAGNETICALLY DILUTED CRYSTAL OF $2K_2\ (Zn,Cu)\ (SO_4)_2\ 6H_2O$

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ABSTRACT. Following the treatment of Polder and Stevens the theory of the crystalline electric field acting on Cu^{++} ion in $K_2Cu(SO_4)_26H_2O$ crystal was developed. From the temperature variation of the magnetic anisotropy (ΔK) of the salt the field parameters were evaluated. Changing the sign of the tetragonal field coefficients and using the same tetragonal field parameters as those of the undiluted salts a good agreement was obtained with the observed values of ΔK for the crystal having .81% Cu^{++} ion.

INTRODUCTION

X-ray studies, magnetic birefringence and optical absorption data on the Tutton salts of iron group of elements point to the existence of an axially distorted octahedral cluster of water dipoles surrounding the paramagnetic ion. The crystal field acting on the paramagnetic ion arises out of this distorted octahedral cluster and the direct and indirect influence of the charges outside this primary cluster. The intensity and asymmetry of this field which depend upon the distribution of electric charges will determine the magnetic anisotropy of the ion. When paramagnetic Tutton Salts are diluted with the corresponding zinc or magnesium Tutton Salt the charge distribution is likely to remain constant except for the distant charges.

Bagguley and Griffiths (1952), however, from paramagnetic resonance experiment came to the conclusion that for diluted copper salt $2K_2{\cdot}(Cu{\cdot}Zn)(SO_4)_26H_2O$, having less than 1% of Cu^{++} ion, the susceptibility at 300°K along the axis of symmetry of the cluster ($K_{\|}$) is smaller than that for directions normal to the symmetry axis ($K_{\perp}$), while at 90°K, $K_{\|}$ is greater than $K_{\perp}$, whereas for the undiluted salts $K_{\|} > K_{\perp}$ at all temperatures.

Mookherji and Lal (1965) from their studies on a magnetically diluted salt of copper (Cu^{++} ion being 0.81%) at different temperatures attempted a qualitative verification of the findings of Bagguley and Griffiths (1952).

In this communication we have tried to explain the temperature variation of the magnetic anisotropy of the diluted salt $2K_2(Zn{\cdot}Cu)(SO_4)_26H_2O$ having

0.81% of Cu^{++} ion, following the crystal field treatment of Polder (1942) and Stevens (1952).

SYMMETRY OF THE CRYSTAL FIELD

Copper potassium sulphate is monoclinic in the space group C_{2h}^5. The unit has the dimension $a, b, c = 9.1$ Å, 12.2 Å and 6.1 Å (Hoffman, 1931) C. There are two magnetically inequivalent paramagnetic clusters in the unit cell. Each cluster consists of a Cu^{++} ion located at the centre of an approximate square formed by four water dipoles. The other two are located centrally above and below this square. The Cu-H_2O distance normal to the square is greater than those in the plane of the square. Thus Cu^{++} ion is at the centre of an ionic cluster which is an approximate octahedron as derived from a regular one by elongating one of its diagonals symmetrically. Hence this octahedron will have very nearly a tetragonal symmetry. Recent PMR measurements by Bose *et al* (1964) show that the departure from tetragonal symmetry is small in this case particularly at low temperatures. As a result the crystal field acting on Cu^{++} ion is predominantly cubic with a small nearly tetragonal component superimposed on it. Now taking the Cu^{++} ion at the origin of a suitably oriented rectangular coordinate system the electric potential of an electron placed at the point (X, Y, Z) in the neighbourhood of the Cu^{++} ion may be represented by (Abragam and Pryce 1951)

$$V(X_i, Y_i, Z_i) = K'(X^4+Y^4+Z^4-\tfrac{3}{5}r^4)+A'(3Z^2-r^2)$$
$$+Q'[5(X^4+Y^4+Z^4-\tfrac{3}{5}r^4)-3(X^4+Y^4-6X^2Y^2)] \quad \ldots (1)$$

where K' is the cubic field coefficient and A' and Q' are those for the tetragonal field.

STARK SPLITTING OF THE GROUND STATE OF THE FREE ION

The ground state of the free Cu^{++} ion is $3d^{9}{}^{2}D_{5/2}$. From group theoretical considerations of Bethe (1929) it is known that the ground state breaks up into two levels in a field of cubic symmetry, while a tetragonal field breaks these levels into four, each of which will have Kramers degeneracy. This degeneracy is lifted only by a magnetic field.

The complete Hamiltonian for the system is

$$H = H^0+V+H_{LS}+H(L+2S),$$

where H^0 is the free ion Hamiltonian, H_{LS} is the spin-orbit interaction $\lambda L.S$. (λ = spin-orbit coupling coefficient) and $H(L+2S)$ is the effect of the magnetic field on the ion.

The matrix elements in the manifold of states spanning $L = 2$ are determined by changing the potential operator as given by equation (1) into its equivalent

angular momentum operator following Stevens (1952). Thus the secular matrix for the ground state is

	2	−2	1	−1	0
2	A_2	B	0	0	0
−2	B	A_2	0	0	0
1	0	0	A_1	0	0
−1	0	0	0	A_1	0
0	0	0	0	0	A_0

where $A_2 = \langle \pm 2 | V | +2 \rangle = -K'\overline{r^4} \frac{2}{105} + \frac{4}{7} A'\overline{r^2} - \frac{10}{105} Q'\overline{r^4}$

$A_1 = \langle \pm 1 | V | \pm 1 \rangle = K'\overline{r^4} \frac{8}{105} - \frac{2}{7} A'\overline{r^2} + \frac{40}{105} Q'\overline{r^4}$

$A_0 = \langle 0 | V | 0 \rangle = -K'\overline{r^4} \frac{12}{105} - \frac{4}{7} A'\overline{r^2} - \frac{60}{105} Q'\overline{r^4}$

$B = \langle \pm 2 | V | 2 \rangle = -K'\overline{r^4} \frac{10}{105} + \frac{70}{105} Q'\overline{r^4}$

Solving this 5×5 matrix we get the energy levels as,

$$\left.\begin{aligned} F_3 &= -6K + 4A + 3Q = A_2 + B \\ F_4 &= +4K + 4A - 4Q = A_2 - B \\ F_5 &= +4K - 2A + 2Q = A_1 \\ F_1 &= -6K - 4A - 3Q = A_0 \end{aligned}\right\} \quad \ldots (2)$$

where $K = \frac{2}{105} K'\overline{r^4}$, $A = \frac{1}{7} A'\overline{r^2}$, $Q = \frac{20}{105} Q'\overline{r^4}$ and $\overline{r^n}$ is the average r^n $(n = 2, 4)$ of the $3d$ electrons.

The corresponding wave functions are,

$$F_3 \rightarrow \tfrac{1}{2}[|2> + |-2>]; \; F_4 \rightarrow \tfrac{1}{2}[|2> - |-2>] \quad \ldots (3)$$
$$F_5 \rightarrow |1> \text{ and } |-1>; \; F_1 \rightarrow |0>$$

Optical absorption findings (Mookherji and Chhonkar 1959) show two peaks and hence to evaluate the three constants K, A and Q we have utilized the mean centres of the energy levels as given by equation 2.

Bose *et al* (1957) have studied the temperature variation of $\Delta K = (K_{\parallel} - K_{\perp})$

for $K_2Cu(SO_4)_26H_2O$ crystals. After many trials the set of parameters which gave the best fit with the observed values of Bose *et al* (1957) are.

$$K = +1460\ cm^{-1},\ Q = -11\ cm^{-1},\ \text{and}\ A = -90\ cm^{-1}.$$

It must be mentioned here that for a correct set of field parameters one should consider the temperature variation of ΔK and not that of the mean moment (Mookherji and Mookherji, 1965 ; Neogy and Mookherji 1965). With the above field parameters the energy levels are

$$F_3 = -9153\ cm^{-1},\ F_1 = -8367\ cm^{-1},\ F_4 = +5524\ cm^{-1},\ F_5 = +5998 cm^{-1}$$

The corresponding wave functions (eq. 3) and the order of energy levels show that F_3 lies lowest as obtained by Polder (1942) but the splittings are widely different. Taking F_3 as zero we have the energy levels as 0, (786), 14677 and 15151 cm^{-1}. The tetragonal separation ($F_5 - F_4$) is 474 cm^{-1}. This agrees well with the optical absorption finding (470 cm^{-1}) of Mookherji and Chhonkar (1959). The other tetragonal separation i.e. $F_3 - F_1 = 786\ cm^{-1}$ is significant.

Now introducing proper spin functions and calculating the spin-orbit and magnetic perturbations we get (Polder)

$$K_{\parallel} = \frac{N\beta^2}{KT}\left(1 - \frac{4\lambda}{F_4 - F_3}\right)^2 + \frac{8N\beta^2}{F_4 - F_3}$$

$$K_{\perp} = \frac{N\beta^2}{KT}\left(1 - \frac{\lambda}{F_5 - F_3}\right)^2 + \frac{2N\beta^2}{F_5 - F_3}$$

From which $K_{\parallel} - K_{\perp} = \frac{N\beta^2}{KT}\left[\left(1 - \frac{4\lambda}{F_4 - F_3}\right) - \left(1 - \frac{\lambda}{F_5 - F_3}\right)\right]^2$

$$+ N\beta^2\left(\frac{8}{F_4 - F_3} - \frac{2}{F_5 - F_3}\right)$$

Substituting the values of $\lambda = -829\ cm^{-1}$, $F_4 - F_3$ and $F_5 - F_3$ the values of ΔK are calculated. These are given in table I along with those observed by Bose *et al* (1957) for comparison.

TABLE I

Anisotropy Compared

	T°K	300	200	100	90
$\Delta K \times 10^6$	Observed	572	829	1573	1734
	Calculated	595	840	1574	1738

The fit may be considered as satisfactory in view of the fact that the tetragonal part of the field has been taken to be the same at all the temperatures. Thermal expansion of the crystal will probably change this part of the field and hence no single suitable set of tetragonal field parameters will be able to provide

an exact fit both at room and at low temperatures. Moreover the findins of Bagguley and Griffith show that above $150°K$ the field has an appreciable rhombic component. The variation of the setting angle with temperature indicates the variation of tetragonal field parameters, it does not indicate the magnitude of the tetragonal part (Bose *et al*, 1961) ; Mookherji and Mathur, 1965).

EFFECT OF MAGNETIC DILUTION

Paramagnetic resonance data (Bagguley and Griffiths, 1952) show that for $K_2Cu(SO_4)_2 6H_2O$ diluted with the corresponding zinc Tutton salt (Cu^{++} less than 1%) $K_{\parallel}$ becomes smaller than $K_{\perp}$ at 300°K and reverse is the case at 90°K; consequently the tetragonal field coefficients will change sign in this diluted salt. According to Van Vleck (1958) this change of sign will effect an inversion of the tetragonal stark levels.

Introducing this change of sign of Q' and A' in equation (1) and treating the crystal field perturbation as before we find that the form of the secular matrix is the same as before but the values of A_1, A_2, A_0 and B are different. Taking $K = 1680$ cm^{-1} and using the same tetragonal field parameters of $CuK_2(SO_4)_2 6H_2O$ crystal (undiluted) the energy levels are given by

$$F_3 = -6K - 4A - 3Q = -9687 \text{ cm}^{-1}$$

$$F_4 = +4K - 4A + 4Q = +7036 \text{ cm}^{-1}$$

$$F_5 = +4K + 2A - 2Q = +6562 \text{ cm}^{-1}$$

$$F_1 = -6K + 4A + 3Q = -10473 \text{ cm}^{-1}$$

The corresponding wave functions remain the same as given by equation (3). Thus F_1 now lies lowest and F_4 is higher than F_5 showing an inversion of tetragonal stark levels with change of sign of the tetragonal field coefficients Q' and A'.

Taking the lowest as zero the energy levels are 0, (786), (17035), (17509) cm^{-1}. The tetragonal separation 474 cm^{-1} in this case also cm^{-1}, is expected as the percentage anisotropy of both the undiluted and diluted salt is ($\simeq 34\%$) the same.

When spin functions α and β corresponding to the components $s_z = \perp \frac{1}{2}$ with respect to z-axis are introduced the ground state $|0>$ is still doubly degenerate. These two states $|0, \frac{1}{2}>$ and $|0, -\frac{1}{2}>$ are modified by the spin orbit coupling the first order as follows :

$$f^+ = \left| 0, \frac{1}{2} \right\rangle - \frac{\lambda}{F_5 - F_0} \cdot \frac{\sqrt{6}}{2} \left| +1, -\frac{1}{2} \right\rangle$$

$$f^- = \left| 0, -\frac{1}{2} \right\rangle - \frac{\lambda}{F_5 - F_0} \cdot \frac{\sqrt{6}}{2} \left| -1, \frac{1}{2} \right\rangle$$

The degeneracy of these two states are lifted by the external magnetic field. On carrying out magnetic field perturbation calculations we get using the well-known formula of Van Vleck,

$$K_{\parallel} = \frac{N\beta^2}{KT} \text{ and } K_{\perp} = \frac{N\beta^2}{KT}\left[1 - \frac{3\lambda}{F_5 - F_1}\right]^2 + \frac{6N\beta^2}{F_5 - F_1}$$

Hence $$K_{\parallel} - K_{\perp} = \frac{N\beta^2}{KT}\left[1 - \left(1 - \frac{3\lambda}{F_5 - F_1}\right)^2\right] - \frac{6N\beta^2}{F_5 - F_1}$$

Thus in this case $K_{\perp}$ becomes greater than $K_{\parallel}$ since λ is negative. The values of $(K_{\perp} - K_{\parallel})$ are calculated and are included in Table II along with the observed values of Mookherji and Lal (1965) for a crystal $2K_2(Cu.Zn)(SO_4)_2 6H_2O$ in which the amount of Cu^{++} ion is 0.81%.

TABLE II

Magnetic anisotropy of diluted salt compared

	T°K	300	200	140	100	90
$(K_{\perp} - K_{\parallel})10^6$	Observed	470	661	1008	1545	−1734
	Calculated	482	678	930	1267	−1740

The fit is satisfactory except at 100°K considering the neglect of variation of the field parameters A, Q with temperature. Thus the set of tetragonal field parameters which explain the magnetic behavior of the undiluted salt can explain also that of the diluted salt containing 0.81% of Cu^{++} ion with their signs changed in the potential function

SPECTROSCOPIC SPLITTING FACTOR

Abragam and Pryce (1951) have calculated the spectroscopic splitting factor g for Cu^{++} ion in the undiluted salt under the influence of a crystal field which is predominantly cubic in symmetry and over which is uperimposed a small tetragonal component. For directions parallel and perpendicular to the tetragonal axis neglecting the square and product terms we have

$$g_{\parallel} = 2 - \frac{8\lambda}{F_4 - F_3} \text{ and } g_{\perp} = 2 - \frac{2\lambda}{F_5 - F_3}$$

Using the values of $(F_4 - F_3)$ and $(F_5 - F_3)$ as deduced from magnetic anisotropy data we get

$$g_{\parallel} = 2.45 \text{ and } g_{\perp} = 2.11$$

These compare well with observed values $g_{\parallel} = 2.45$ and $g_{\perp} = 2.05$ (Bleaney *et al*, 1949).

Now coming to the case of diluted crystal of $2K_2(Cu\ Zn)(SO_4)_2 6H_2O$ having less than 1% of Cu^{++} ion, $g_{\|}$ and $g_{\perp}$ as calculated by Bagguley and Griffiths (1952) are given by.

$$g_{\|} = 2.0 \text{ and } g_{\perp} = 2 - \frac{6\lambda}{F_5 - F_1}$$

Substituting for $F_5 - F_1$ as deduced from magnetic anisotropy data gives $g_{\|} = 2.0$ and $g_{\perp} = 2.29$. These compare favourably with paramagnetic resonance data (2.05 and 2.26).

Further improvement on the theory including covalency factors is in progress in this laboratory.

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